

C13 --Six isomers are possible for difunctional, incompletely condensed POSS nanostructures  $[(\text{RSiO}_{1.5})_4(\text{RXSiO}_{1.0})_2]_{\Sigma 6}$  as shown in Scheme 9.--

Please replace the paragraph "Figure 10. Isomers for difunctional, incompletely condensed POSS nanostructures  $[(\text{RSiO}_{1.5})_4(\text{RSiO}_{1.0})_2]_{\Sigma 6}$ " at the bottom of page 18 to -- Scheme 9--.

### REMARKS

In the Office Action, dated April 11, 2002, the Examiner alleged that the previously filed amendment did not meet the requirement of 37 CFR 1.121 with respect to the amendments made in the Specification section. Specifically, the Examiner alleged that the previously filed amendment did not include clean and marked-up versions of the replacement paragraphs. These replacement paragraphs have been provided herein. No new matter has been added.

As it is believed that all of the Examiner's objections and rejections have been overcome, it is respectfully requested that the application be allowed to issue.

If the Examiner has any questions regarding the foregoing, or if the Examiner believes that an interview would facilitate the examination of this application, or if any additional information is required, the Examiner is invited to contact the undersigned at (415) 983-1280.

Respectfully submitted,  
PILLSBURY WINTHROP L.L.P.

Dated: May 3, 2002

By: Karry W. Wang  
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### **CERTIFICATE OF MAILING**

I hereby certify that this correspondence is being deposited with the United States Postal Service, postage prepaid, in an envelope addressed to Commissioner of Patents, Washington D.C. 20231-9999 on 05/03/02

Date: May 3, 2002 By: [Signature]

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**APPENDIX**  
**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

**IN THE SPECIFICATION:**

**The specification is changed as follows (text which has been struck through has been deleted and underlined text \_\_\_\_\_ has been added):**

Paragraph beginning at line 1 of page 2 has been amended as follows:

Prior art has reported that bases (e.g., NaOH, KOH, etc.) could be used to both catalyze the polymerization of POSS into lightly networked resins or to convert selected polysilsesquioxane resins into homoleptic polyhedral oligomeric silsesquioxane structures. Marsmann et al have more recently shown that a variety of bases can be used to redistribute smaller homoleptic POSS cages into larger sized homoleptic cages. (Marsmann, H.C. and Rikowski, E., Polyhedron, 1997, 16, 3357-3361). While there is precedent in the literature for treatment of silsesquioxanes and POSS systems with base, the previous art does not afford the selective manipulation of silicon-oxygen frameworks and the subsequent controlled production of POSS fragments, homoleptic POSS nanostructures. Furthermore, the prior art does not provide methods of producing POSS systems suitable for functionalization and subsequent polymerization or grafting reactions. This oversight in the prior art is reflective of the fact that the invention of POSS-based reagents, monomers and polymer technology has only recently been developed and consequently post-dates this prior art. Hence POSS compositions and processes relevant to the types of systems desired for POSS monomer/polymer technology were not envisioned in the prior art. Additionally the prior art does not demonstrate the action of bases on silane, silicate, or silsesquioxane feedstocks suitable for producing low-cost and high purity POSS systems.

Paragraph beginning at line 18 of page 2 has been amended as follows:

In contrast to the prior art (~~Brown et al. and Marsmann et al.~~ see, e.g., Brown, J.F., Vogt, L.H., and P.I. Prescott J., Am. Chem. Soc. 1964, 86, 1120-1125; Marsmann, H.C. and

Rilowski, E., Polyhedron, 1997, 16, 3357-3361), the processes taught here specifically enable the development of lower cost, high purity POSS systems bearing functionalities useful as derivitizable chemical reagents and feedstocks.

Paragraph on the top of page 5 has been deleted:

~~Figure 1. Examples of Common Silsesquioxane, Silicate, POSS Nanostructures and Fragments.~~

Paragraph near the top of page 9 has been amended as follows:

~~Figure 2. Illustration of Process I where polymeric silsesquioxane resins are converted into POSS fragments and nanostructures~~Scheme 1.

Paragraph beginning at line 1 of page 9 has been amended as follows:

For the above reaction scheme (Scheme 1) the polymeric silsesquioxane resin is converted into either Poss fragments or nanostructured POSS cage species depending on the type of base and conditions employed. The conversion of polysilsesquioxanes  $[\text{RSiO}_{1.5}]_{\infty}$  to POSS-species (homoleptic  $[(\text{RSiO}_{1.5})_n]_{\Sigma\#}$ , functionalized homoleptic  $[(\text{RSiO}_{1.5})_m(\text{RXSiO}_{1.0})_n]_{\Sigma\#}$ , heteroleptic  $[(\text{RSiO}_{1.5})_m(\text{RSiO}_{1.5})_n]_{\Sigma\#}$  and functionalized heteroleptic  $[(\text{RSiO}_{1.5})_m(\text{RXSiO}_{1.0})_n]_{\Sigma\#}$  or into POSS-fragments  $[(\text{RXSiO}_{1.5})_n]$  can be selectively controlled through manipulation of the process variables discussed above. The process can be conducted using a polysilsesquioxane resin which may contain only one type of R group to produce homoleptic  $[(\text{RSiO}_{1.5})_n]_{\Sigma\#}$  products. Alternatively the process can be carried out using polysilsesquioxane resins containing more than one type of R group or with mixtures of polysilsesquioxanes in which each contains different R groups to afford heteroleptic  $[(\text{RSiO}_{1.5})_m(\text{R}'\text{SiO}_{1.5})_n]_{\Sigma\#}$  products. For the above reaction scheme (Scheme 1) in which mixtures of homoleptic POSS cages (i.e. R of one POSS cage  $\neq$  R of the second POSS cage) are substituted for the polysilsesquioxane resin the process effectively converts mixtures of homoleptically substituted POSS cages into heteroleptic POSS cages (functionalized and nonfunctionalized) that contain statistical distributions of different R groups per cage. In most cases the POSS fragments and various homo or heteroleptic nanostructured POSS species can be separated from one another through crystallization, or extractions by utilizing the differences in solubility between the reaction products and the starting silsesquioxane.

Paragraph beginning at line 8 of page 10 has been amended as follows:

The process developed utilized bases (as defined previously) to convert fragments and functionalized POSS nanostructures  $[(\text{RSiO}_{1.5})_m(\text{RXSiO}_{1.0})_n]_{\Sigma\#}$  into alternate functionalized POSS nanostructures  $[(\text{RSiO}_{1.5})_m(\text{RXSiO}_{1.0})_n]_{\Sigma\#}$ . In the process a POSS fragment is dissolved or suspended in acetone, benzene or alcoholic solvents after which a solution of base is added with stirring. In general the reaction conditions employed in this process are milder than those used in Process I and can utilize both hydroxide and nonhydroxide bases, while the molar ratio of base relative to silicon is 1:10 (with 1:1 or 1:2 ration being preferred). Scheme 2 below illustrates some examples of the conversion of POSS fragments into POSS cages.

Paragraph at the bottom of page 10 has been amended as follows:

~~Figure 3. POSS Fragments converted into POSS cages~~Scheme 2.

Paragraph beginning at line 8 of page 11 has been amended as follows:

When mixtures of POSS fragments are utilized they are incorporated statistically into the POSS structure and their final composition is based on the stoichiometry of the starting POSS fragments. In some cases the statistical degree of substitution between these groups is governed by isomorphism resulting from the nearly identical topological shape of the R group (e.g. vinyl and ethyl). Isomorphic governance is often observed for closely related R groups (e.g. allyl and propyl etc.); however, on occasion the trend is not followed due to other factors such as rate of reaction, reagent addition, or solubility between various POSS fragments and products. For example the reaction of 1 equivalent of EthylundeconoateSi(OMe)<sub>3</sub> or VinylSi(OMe)<sub>3</sub> with 7 equivalents of MeSi(OMe)<sub>3</sub> results in a molecule of formula 2 of the composition  $[(\text{ViSiO}_{1.5})_1(\text{MeSiO}_{1.5})_7]_{\Sigma 8}$  or  $[(\text{EthylundeconoateSiO}_{1.5})_1(\text{MeSiO}_{1.5})_7]_{\Sigma 8}$  despite the topological dissimilarity between the R groups.

Paragraph beginning at line 27 of page 11 has been amended as follows:

~~Figure 4~~Scheme 3 illustrates actual reactions that use the conditions described in Process II as proof that the bases and conditions described in Process II are effective for the conversion of functionalized POSS cages (i.e.  $[(\text{RSiO}_{1.5})_m(\text{RXSiO}_{1.0})_n]_{\Sigma\#}$ ) desired POSS structures. It should also be noted that in most cases ~~these~~this process results in an increase

in the number of functionalities (X) on a POSS nanostructure while at the same time maintaining the original number of silicon atoms contained within the starting nanostructural framework. This can be desirable for a variety of subsequent synthetic product manipulations and derivations.

Please delete the paragraph beginning at page 11, line 34:

~~Figure 4 illustrates actual reactions that use the conditions described in Process II as proof that the bases and conditions described in Process II are effective for the conversion of functionalized POSS cages (i.e.  $[(\text{RSiO}_{1.5})_m(\text{RXSiO}_{1.0})_n]_{\text{Si}}$ ) desired POSS structures. It should also be noted that in most cases these process results in an increase in the number of functionalities (X) on a POSS nanostructure while at the same time maintaining the original number of silicon atoms contained within the starting nanostructural framework. This can be desirable for a variety of subsequent synthetic product manipulations and derivations.~~

Paragraph beginning at the middle of page 12 has been amended as follows:

~~Figure 4. POSS Cages being interconverted~~Scheme 3.

Paragraph beginning at the second line 1 of page 12, after Scheme 3, has been amended as follows:

The first example in ~~Figure 4~~Scheme 3 illustrates the selectivity for the cleavage of 6 membered silicon-oxygen rings in the presence of 8 membered silicon-oxygen rings by the base, to afford the trifunctionalized POSS species. This reaction is driven by the release of greater ring strain energy from the cleavage of the 6 membered silicon-oxygen ring vs. cleavage of the 8 membered silicon-oxygen ring and is thermodynamically favorable. In the second example the energy of the twisted conformation is relieved upon cleavage to form a more open structure.

Paragraph beginning at the top of page 14, after the two reaction schemes, has been amended as follows:

~~Figure 5. Silsesquioxane/siloxane fragments being inserted into POSS Cages~~Scheme 4.

Paragraph beginning at line 1 of page 14 has been amended as follows:

Scheme 4 above illustrates examples of Silsesquioxane/siloxane fragments being inserted into POSS cages. The net reaction in the examples shown in ~~Figure 5~~Scheme 4 is cleavage of an Si-O-Si bond in the POSS or POSS silicate nanostructure and insertion of the POSS fragment. This reaction results in the expansion of the silicon-oxygen ring in the POSS nanostructured product. Note that the ring expansion in these reactions is in some cases favored thermodynamically through relief of ring strain in the silsesquioxane starting material. For example, the reaction of 1 equivalent of Vinyl(OMe)<sub>3</sub> with  $[(c-C_6H_{11})SiO_{1.5}]_6 \Sigma_6$  results in POSS molecule having the composition  $[(c-C_6H_{11}(SiO_{1.5})_4(c-C_6H_{11})(HO)SiO_{1.0})_2(ViSiO_{1.0})_1] \Sigma_7$ .

Paragraph beginning at line 8 of page 15 has been amended as follows:

Homoleptic POSS nanostructures  $[(RSiO_{1.5})_n] \Sigma_n$  are readily converted into POSS nanostructures having the formula  $[(RSiO_{1.5})_m(RXSiO_{1.0})_n] \Sigma_n$ , as well as POSS fragments having the formula  $RSiX_3$ ,  $[(RXSiO_{0.5})_n]$ ,  $[(RXSiO_{1.0})_n]$ , or  $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]$  through the use of bases as shown in ~~Figure 6~~Scheme 5. Note that all possible geometric and stereochemical isomers for each product are not shown.

Paragraph beginning at toward the bottom of page 15 has been amended as follows:

~~Figure 6. Illustration of Process III~~Scheme 5.

Paragraph beginning at second line 1 of page 15, at the bottom of the page, has been amended as follows:

Furthermore as a variation of this process it is possible to interconvert various sizes of POSS nanostructures. For example, with the proper addition of base  $[(RSiO_{1.5})_6] \Sigma_6$  can be either cleaved into a smaller POSS fragments (e.g.  $RSiX_3$ ,  $[(RXSiO_{0.5})_n]$ ,  $[(RXSiO_{1.0})_n]$ , or  $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]$ ) or functionalized into heteroleptic POSS nanostructures of the same size (e.g.  $[(RSiO_{1.5})_4(RXSiO_{1.0})_2] \Sigma_6$ ) or larger (e.g.  $[(RSiO_{1.5})_4(RXSiO_{1.0})_3] \Sigma_7$ ) as shown in ~~Figure~~Scheme 6.

Paragraph beginning at the middle of page 16 has been amended as follows:

~~Figure 7. Illustration of Process III~~Scheme 6.

Paragraph beginning at the second line 1 of page 16, toward the bottom of the page, has been amended as follows:

As a variation of the above it is recognized that this process can utilize mixtures and distributions of POSS cages as well as polyhedral oligomeric silicate species (e.g.  $[(\text{CH}_3)_3\text{SiO}]\text{SiO}_{1.5}]_6$ ,  $[(\text{CH}_3)_4\text{NO}]\text{SiO}_{1.5}]_6$ ,  $[(\text{CH}_3)_3\text{SiO}]\text{SiO}_{1.5}]_8$ ,  $[(\text{CH}_3)_4\text{NO}]\text{SiO}_{1.5}]_8$ . In such cases the base effectively converts cages of several sizes into functionalized and nonfunctionalized heteroleptic POSS nanostructures as shown in ~~Figure~~Scheme 7. This represents an entirely new synthetic route for the preparation of the very useful incompletely condensed trisilanol reagents  $[(\text{RSiO}_{1.5})_4(\text{RXSiO}_{1.0})_3]_{\Sigma 7}$  in particular where  $X = \text{OH}$ .

Paragraph beginning before line 1 of page 17 has been amended as follows:

~~Figure 8. Illustration of the conversion of POSS and Silicate Nanostructures—Process III~~Scheme 7.

Paragraph beginning at line 1 of page 17 has been amended as follows:

A final variation of this process is the selective action of base on heteroleptic POSS nanostructures (see Scheme 8). POSS nanostructures bearing more than one type of R group per cage  $[(\text{RSiO}_{1.5})_m(\text{RSiO}_{1.5})_n]_{\Sigma \#}$  are readily converted through the use of base into functionalized POSS nanostructures  $[(\text{RSiO}_{1.5})_m(\text{RXSiO}_{1.0})_n]_{\Sigma \#}$ . Note that all possible geometric and stereochemical isomers are not shown.

Paragraph beginning at the bottom of page 17 has been amended as follows:

~~Figure 9. Illustration of the conversion of POSS Nanostructures—Process III~~Scheme 8.

Paragraph beginning at line 18 of page 18 has been amended as follows:

Six isomers are possible for difunctional, incompletely condensed POSS nanostructures  $[(\text{RSiO}_{1.5})_4(\text{RXSiO}_{1.0})_2]_{\Sigma 6}$  as shown in ~~Figure 10~~Scheme 9.

Paragraph beginning at the bottom of page 18 has been amended as follows:

Figure 10. Isomers for disfunctional, incompletely condensed POSS nanostructures  
 $[(\text{RSiO}_{1.5})_4(\text{RSiO}_{1.0})_2]_x$  Scheme 9.